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The Mechanism of Mechanical Alloying

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The mechanical alloying process is a new method for producing composite metal powders with controlled microstructures. It is unique in that it is an entirely solid state process, permitting dispersion of insoluble phases such as refractory oxides and addition of reactive alloying elements such as aluminum and titanium. Interdispersion of the ingredients occurs by repeated cold welding and fracture of free powder particles. Refinement of structure is approximately a logarithmic function of time, and depends on the mechanical energy input to the process and work hardening of the materials being processed. A condition of steady state processing is eventually achieved marked by saturation (constant) hardness and constant particle size distribution, although structural refinement continues. Evidence of this is presented, and the nature of the cold welding and characteristics of the processed powder are described.

THE mechanical alloying process was developed as a means of combining the advantages of γ' precipitation hardening for intermediate temperature strength and oxide dispersion strengthening for high-temperature strength in a nickel-base superalloy, IN-853.[1] However, the process is also applicable to a large number of systems which, due to liquid- or solid-phase segregation, high melting temperature, or very high reactivity, are not amenable to production by conventional techniques.

In the mechanical alloying process a blend of powders is subjected to highly energetic compressive impact forces such as those occurring in a high energy stirred ball mill, shaker mill or vibratory ball mill. Interdispersion of the ingredients occurs by a process involving cold welding and fracture of the powder particles. In alloy manufacture the starting charge usually consists of a blend of elemental, master alloy, and compound powders of very different characteristics and initial particle sizes, making it difficult to follow the process quantitatively. The present study utilizes a two-component system of elemental powders with identical and very narrow initial particle size ranges. This enables a more quantitative description of the development of composite powder particles and the mechanism of their production.

EXPERIMENTAL PROCEDURES

The chromium powder used in this study was prepared by alumino-thermic reduction and grinding, resulting in an angular particle morphology. The iron powder was water atomized and possessed a rounded particle shape. Both powders were screened to -140, $+200$ mesh to give a very narrow starting size range. The processing medium consisted of 0.79 cm diam 52100 alloy steel balls, etched 10 min. in HCl to provide a roughened surface and washed in water and acetone. Process charges consisted of 7.48 grams of a mixture of 50 vol pct each of the chromium and iron powders and 22 (44 grams) of the etched steel balls.

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Processing was performed in a small, high speed shaker mill. Each charge was milled for a specified time over the range 0.5 to 200 min. The mill jar was sand blasted and washed in acetone between runs.

The processed powders were screen analyzed and the -80, $+100$ mesh and -325 mesh powder screen fractions were mounted in thermosetting epoxy. The mounts were sectioned such that any plate-shaped powder particles would be viewed in edge section after polishing. Samples of the steel balls were nickel plated, sectioned and polished for metallographic examination of the cold welded layers on their surfaces.

Microhardness measurements were made on the -80, $+100$ mesh powder size fraction and on the layers welded to the surfaces of the balls. The average of ten measurements was taken for each data point. Measurements were made of the thickness of the deformed powder particles and of lamellae within composite particles in this size range.

RESULTS AND DISCUSSION

One way of following the mechanical alloying process is by considering it as a sequence of time periods characterized by important events or powder properties. For the purposes of this paper the process has been broken down into five time intervals: 1) Initial period; 2) Period of welding predominance; 3) Period of equiaxed particle formation; 4) Start of Random Welding Orientation; 5) Steady State Processing. These periods are defined in terms of: a) powder size distribution and shape, b) internal structure of powder and material on ball surface, c) hardness of material on ball surfaces and of coarse powders, d) division of material between ball surfaces and free powders. Finally, a model is proposed to account for the observed rate of structural refinement.

Initial

The first twelve minutes of processing, exemplified by the structure at 4.5 min., are characterized by the development of a thin welded layer on the balls consisting of one or two particle thicknesses (see Fig. 1(*a*)) and the development of both coarser and finer particles than present in the initial powder charge (see Figs. 1(*b*) and 1(*c*)). Powder particles

Fig. 1—Structure of powder processed 4.5 min. (*a*) Layers welded to ball surface. (*b*) −80, +100 mesh screen fraction. (*c*) −325 mesh screen fraction.

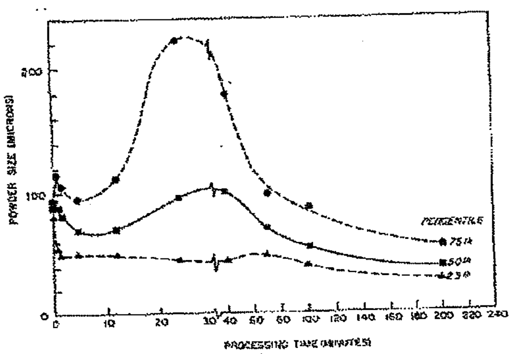

Fig. 2—Powder size distribution as a function of processing time.

within the coarser fraction initially consist of plates formed by flattening of equiaxed starting particles and are of the same volume as the initial powder particles. Toward the end of this period an increasing number of composite particles with the different ingredients arranged in parallel layers also appear in the coarser size fractions.

The particles first appearing in the −325 mesh fraction are predominantly equiaxed and represent fragments of the more friable particles within the starting mix. The proportion of platelike particles in this size fraction increases with time as the equiaxed particles are affected a second time or as fragments of larger particles enter the −325 mesh fraction. The powder size distribution (see Fig. 2) does not change drastically during this time period and

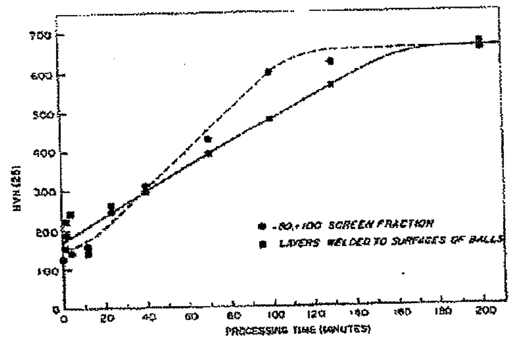

Fig. 3—Microhardness of the −80 +100 mesh powder screen fraction and the layers welded on the surfaces of the balls as a function of processing time.

both powder particles and welded layers remain relatively soft and ductile (see Fig. 3). The hardness data are widely scattered as would be expected early in a statistical process. The amount of powder welded to the ball surface during this time period, indicated by the difference in the ball weight before and after processing, is only about one percent of the total powder charge.

Period of Welding Predominance

During the period from 12 to 30 min., as exemplified by material at 23.5 min., there is a substantial increase in the relative amounts of the coarser size fractions while the amount of the finer fractions remains approximately constant (see Fig. 2). Both the welded layer on the balls and the coarser size fractions display a multilayered composite structure with lamellae running parallel to the ball surfaces or the long axis of the flake particles (see Figs. 4(*a*) and 4(*b*)).

The coarse powders are plate-shaped, having individual volumes much smaller than equiaxed particles of a similar mesh size. At 23.5 min. the average thickness of the plate-shaped composite particles in the −80, +100 mesh fraction is about 25 μm. The average volume of these particles, 6.6×10^5 μm^3, is only 15 pct of that of an equiaxed particle of the same mesh size and is nearly identical to that of the −140, +200 mesh elemental starting powders, 7×10^5 μm^3. The individual elemental lamellae within these composite particles must therefore be much smaller in volume than the initial elemental powder particles, and thus must be comminuted fragments of the elemental starting powders.

The structures of the coarser powder fractions and the layers welded to the ball surfaces are similar (compare Figs. 4(*a*) and 4(*b*)). This similarity indicates either an interchange between the welded layer and free powder or that material on the ball surfaces continued to be processed at about the same rate as free powder.

The fine particles on the other hand remain elemental but are now predominantly flake-shaped, lagging behind the developing structure of both the coarser powder fractions and the layers welded to the ball surfaces. These fine powder particles are

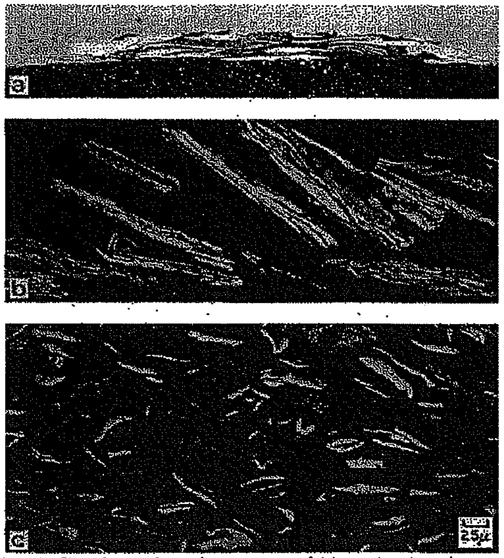

Fig. 4—Structure of powder processed 23.5 min. (*a*) Layers welded to ball surface. (*b*) −80, +100 mesh screen fraction. (*c*) −325 mesh screen fraction.

probably pieces fractured from the edges of the coarser composite particles and which were not cold welded to other lamellae.

The hardness shows a substantial increase over that of the starting powders (see Fig. 3) as virtually all material has been severely deformed.

Period of Equiaxed Particle Formation

In the processing time period between roughly 30 and 60 min. there is a sharp decrease in the amount of very coarse plate-like particles (see Fig. 2) and a trend toward more equiaxed dimensions (see Fig. 5(*b*)). A similar change occurs in the layer welded to the balls (Fig. 5(*a*)). This is probably a result of a significant decrease in ductility of the composite powder particles, which is associated with the achievement of a hardness of about 300 kg/mm^2.

The change in the structure of the −325 mesh powder particles, however, is much more startling (see Fig. 5(*c*)) and is marked by the virtual disappearance of elemental powder fragments and the appearance of composite particles consisting of parallel lamellae of a structure similar to those of the coarser powders. These powder particles have originated from the comminution of similarly structured particles within the coarser size fractions. At the same time, the smaller elemental flake-like particles have mostly been captured by welding to other particles.

In spite of the lower ductility the amount of powder welded to the balls increased to about 4 pct.

Start of Random Welding Orientation

In the processing time period between 60 and 100 min. the elemental lamellae of both the welded layer

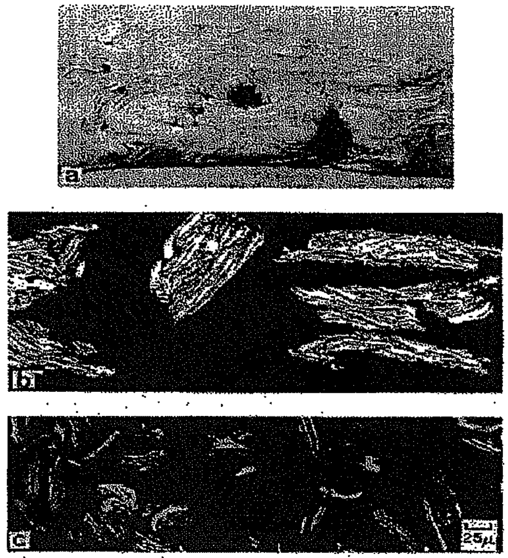

Fig. 5—Structure of powder processed 40 min. (*a*) Layers welded to ball surface. (*b*) −80, +100 mesh screen fraction. (*c*) −325 mesh screen fraction.

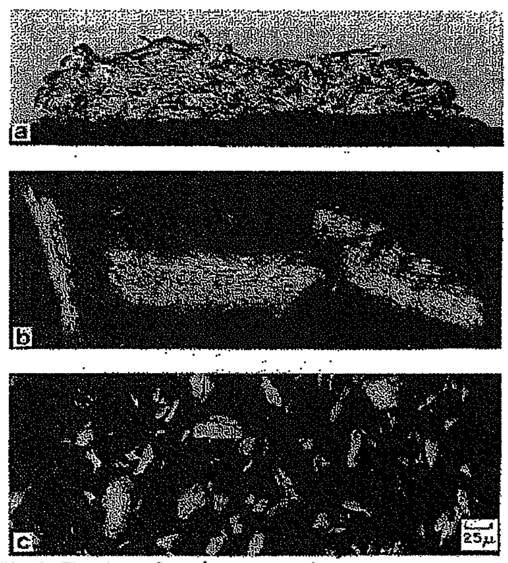

Fig. 6—Structure of powder processed 70 min. (*a*) Layers welded to ball surface. (*b*) −80, +100 mesh screen fraction. (*c*) −325 mesh screen fraction.

and the coarser powder fraction become convoluted rather than being linear (see Figs. 6(*a*) and 6(*b*). There is a similar tendency toward convolution of the lamellae in the finer powder fraction but this is dif-

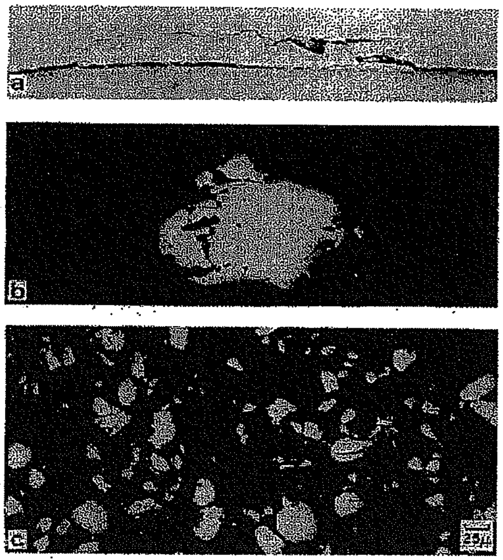

Fig. 7—Structure of powder processed 200 min. (*a*) Layers welded to ball surface. (*b*) −80, +100 mesh screen fraction. (*c*) −325 mesh screen fraction.

ficult to see because of their small size and relatively equiaxed shape. The appearance of this convoluted structure is due to welding together of equiaxed powder particles without any particular preference to the orientation with which they weld. At earlier stages in the process, flake-like particles tend to reweld with their long axes parallel.

Within this period of processing time, there is a substantial increase in the hardness of the material and concurrent decrease in the proportion of coarser sizes in the loose powder as the ductility of the powder continues to decrease. The proportion of powder welded to the balls, however, increases to a maximum of about 6 pct toward the end of this period. This is probably related to the gradual depletion of oxygen in the milling atmosphere due to adsorption by the fresh metal surfaces created during processing. This change in the milling atmosphere favors welding to the balls.

At this point, the welded layer on the balls is quite thick and its hardness lags behind that of the coarse powder by as much as 100 kg/mm^2 (see Fig. 3), or by as much as 40 min. in processing time. Statistical evaluation of variance from the means (F test) indicates a greater than 98 pct probability that this difference in the average hardnesses did not occur by chance.

This observation together with the smallness of the amount of the material welded to the balls implies that plastic deformation and cold welding occur predominantly by the compression of free particles between colliding balls rather than by the addition of particles to the welded surface layers followed by dewelding to give coarser composite particles.

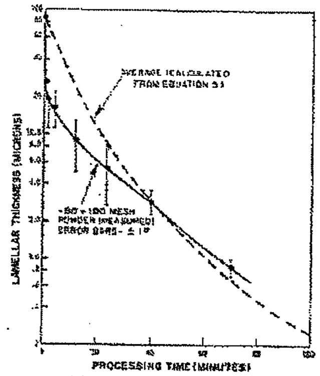

Fig. 8—Variation of lamellar thickness with processing time.

Steady-State Processing

For processing times of longer than 100 min. the product is characterized by increasing internal homogeneity of all the powder size fractions (see Fig. 7) to a degree that can no longer be followed optically. The powder particle size has reached a steady-state distribution which is dependent upon the composition of the system and of the processing parameters (see Fig. 2). The hardnesses of the free powder and the welded layer on the surfaces of the balls reach saturation at about 650 kg/mm^2 (see Fig. 3) and the amount of material welded to the balls decreases to around one percent.

Structural Refinement Rate and Energy Considerations

During the initial period of processing a wide variety of structures exist in the mechanically alloyed powders. Powders which have been trapped between colliding balls are severely deformed while a portion of the powder remains relatively unaffected. This makes determination of the average refinement rate at early times in the process very difficult.

One valuable piece of information on the amount of deformation required to cold weld can be obtained for the powders at this stage however. The −80, +100 size fraction was selected for this purpose since no undeformed powder particles can appear in it. All particles which have escaped being acted upon by the balls or which have been acted upon and fragmented will pass through a 100 mesh screen. However particles of the initial 74 to 105 μm starting material which have been deformed about 50 to 85 pct to discs without fracturing will be retained between the 80 and 100 mesh screens. The average lamellar thickness in this coarse size fraction in the first few minutes of processing (see Fig. 8) indicates that a powder particle is reduced in thickness from about 89 μm to about 25 μm in a single collisional event. This thickness decrease of around 3 to 1 is sufficient to cause cold welding in many cases where overlapping particles are trapped.[2] When these particles are of different constituents, as would be true statistically one-half of the time, a composite plate results (see Fig. 1(*b*)).

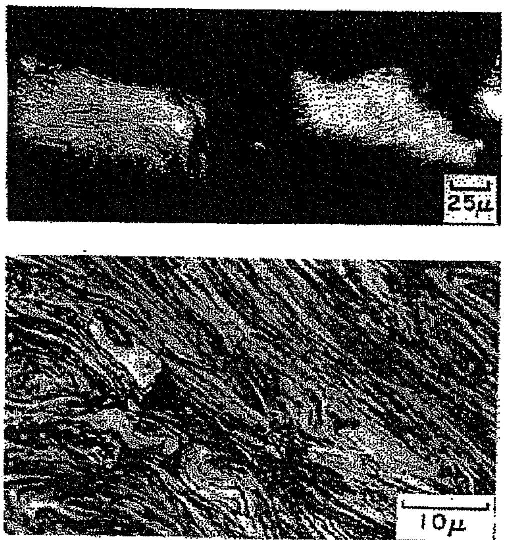

Fig. 9—Microstructure of the −80, +100 mesh fraction of the powder processed 100 min.

With increased processing time, the structural differences between the size fractions are gradually eliminated. At 40 minutes the coarse and fine fractions are identical in appearance (compare Figs. 5(*b*) and 5(*c*)). The average lamellar thickness has been reduced to about 3 μm at this point. Prior to this time the overall average lamellar thickness is greater than that of the −80, +100 mesh size fraction since there are significant amounts of material in the finer fractions processed to a lesser degree (see, for example, Fig. 4(*c*)).

The average rate of change of lamellar thickness can be calculated if certain assumptions are made concerning the energetics and statistics of the process. First, assume that the rate at which material is trapped between colliding balls is independent of time. This assumption is fairly good since the vibration rate of the mill is constant, the number of balls is fixed, the ball diameter is always at least ten times the maximum powder particle diameter and the amount of powder welded to the balls was always less than 7 pct. Therefore, the energy input rate to the process is constant.

$$\frac{dE}{dt} = K_1 \qquad [1]$$

where E = energy
t = time

Next assume that the energy required per unit strain for a constant volume of material is a linear function of the instantaneous Vickers' hardness of the powder.

$$\frac{dE}{d\epsilon} = K_2 H \qquad [2]$$

where ϵ = true strain = $\ln \frac{L_0}{L}$
L = lamellar thickness

During the first 100 min. of processing the Vickers hardness can be approximated by

$$H = 125 + 4.57\,t \qquad [3]$$

Combining Eqs. [1], [2] and [3] and combining constants K_1 and K_2 we obtain:

$$\frac{d\epsilon}{dt} = \frac{K_3}{125 + 4.57\,t} \qquad [4]$$

The strain, ϵ, as function of time is obtained by integrating over time:

$$\epsilon = \frac{K_3}{4.57} \ln(1 + 0.0365\,t) \qquad [5]$$

The value of the system constant K_3 is calculated from the data at 40 min. where $L_0 = 89$ μm and $L = 2.85$ μm. This value, 17.5, was used to calculate the lamellar thickness at other times shown in Fig. 8. As expected, the average initial rate of refinement is slower than that of the −80, +100 mesh size range.

The predicted lamellar thickness at 70 min., 0.69 μm, is exactly the resolving power of the optics used to take the photomicrograph of Fig. 6. Examination of the −80, +100 mesh particles in Fig. 6(*b*) indicate that more than half of the lamellae are indeed poorly resolved. The measured lamellar thickness, 0.87 μm, is, therefore, in reasonably good agreement with the prediction. At 100 min. (see Fig. 9) substantially all the lamellae in the −80, +100 mesh fraction are unresolved as expected.

SUMMARY AND CONCLUSIONS

The following conclusions concerning the mechanical alloying process can be drawn from the example used in this paper:

1. Formation of composite particles and refinement of structure appears to occur predominantly by cold welding and fracturing of free powder particles.
2. Homogeneity of composite particles is approximately a logarithmic function of time. The rate of structural refinement is dependent upon the rate of mechanical energy input to the process and the work hardening rate of the material being processed.
3. The mechanical alloying process can be divided into five stages: The initial period, the period of welding predominance, the period of equiaxed particle formation, the start of random welding orientation, and steady-state processing.
4. Variability of homogeneity from one composite particle to another is eliminated in about one-third of the time marking the beginning of steady state processing.
5. The onset of steady state processing is associated with the achievement of saturation hardness and constant particle size distribution. Structural refinement continues into the steady state processing period.

The example given in this paper is an artificial one constructed for the ease of understanding the development of mechanically alloyed structures. In practice, the variety and size range of raw materials would be much greater. The specific times to develop a given structure in any system would be a function of the initial particle sizes and characteristics of the ingredients as well as the particular apparatus

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involved for carrying out the process and the operating parameters of this apparatus. In addition, the endpoint microstructure would be a function of the application for which the alloy is desired.

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